

## STATEMENT

I, Satoshi OHGUSHI—hereby declare that I am conversant in both Japanese and English languages and that I believe the following is a true and correct translation of the Japanese Patent Application No. 2004-369733.

Date: September 10, 2010

A handwritten signature in cursive script, reading "Satoshi Ohgushi", written in black ink on a white background.

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**JAPAN PATENT OFFICE**

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[Name of Article] Abstract 1

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[Claim 1]

A rubber composition which is a high-hardness compounded rubber composition comprising 100 parts by weight of a rubber component made of (a) from 20 to 80 % by weight of a vinyl-cis-polybutadiene rubber containing 1,2-polybutadiene having a melting point of 170 °C or higher and a high-molecular substance having at least one unsaturated double bond per a repeating unit and comprising at least one member selected from polyisoprene, crystalline polybutadiene having a melting point of not higher than 150 °C, liquid polybutadiene and derivatives thereof and (b) from 80 to 20 % by weight of a diene-based rubber other than (a); and (c) from 60 to 100 parts by weight of a rubber reinforcing agent, which is characterized in that the 1,2-polybutadiene is dispersed in a short crystalline fiber state and the high-molecular substance is dispersed in a granular state in the cis-polybutadiene rubber which is a matrix component of said vinyl-cis-polybutadiene rubber (a); and that the short crystalline fiber of the 1,2-polybutadiene is dispersed in particles of the high-molecular substance.

[Claim 2]

The rubber composition which is a high-hardness compounded rubber composition according to claim 1, which is characterized in that said vinyl-cis-polybutadiene rubber (a) is produced by a process for producing a vinyl-cis-polybutadiene rubber by subjecting 1,3-butadiene to cis-1,4-polymerization in a hydrocarbon-based solvent by using a cis-1,4-polymerization catalyst, subsequently making a 1,2-polymerization catalyst copresent in the resulting polymerization reaction mixture to subject the 1,3-butadiene to 1,2-polymerization, thereby forming 1,2-polybutadiene having a melting point of 170 °C or higher, and then separating, recovering and obtaining a vinyl-cis-polybutadiene rubber as formed from the resulting polymerization reaction mixture, which is characterizing by including a step for adding a high-molecular substance having at least one unsaturated double bond per a repeating unit within the production system of the vinyl-cis-polybutadiene rubber.

[Claim 3]

The rubber composition which is a high-hardness compounded rubber composition according to claim 1 or 2, which is characterized in that in the production step of the vinyl-cis-polybutadiene rubber (a), the unsaturated high-molecular substance is contained in the range of from 0.01 to 50 % by mass based on the total sum of the crystalline fiber of 1,2-polybutadiene and the cis-polybutadiene rubber.

[Claim 4]

The rubber composition which is a high-hardness compounded rubber composition according to any one of claims 1 to 3, which is characterized in that the short fiber of 1,2-polybutadiene in said vinyl-cis-polybutadiene rubber (a) is also dispersed in the cis-polybutadiene rubber as the matrix component without being contained in the particles of the high-molecular substance; that the major axis length of the short crystalline fiber dispersed in said matrix is in the range of from 0.2 to 1,000  $\mu\text{m}$ ; and that the major axis length of the short crystalline fiber of the 1,2-polybutadiene dispersed in the particles of said high-molecular substance is in the range of from 0.01 to 0.5  $\mu\text{m}$ .

[Claim 5]

The rubber composition which is a high-hardness compounded rubber composition according to any one of claims 1 to 4, which is characterized that said vinyl-cis-polybutadiene rubber (a) has the following characteristics:

(1) the cis-polybutadiene rubber which is the matrix component of said vinyl-cis-polybutadiene rubber has a Mooney viscosity in the range of from 10 to 50;

(2) the cis-polybutadiene rubber which is the matrix component of said vinyl-cis-polybutadiene rubber has a viscosity in a toluene solution at 25 °C in the range of from 10 to 150;

(3) the cis-polybutadiene rubber which is the matrix component of said vinyl-cis-polybutadiene rubber has an  $[\eta]$  in the range of from 1.0 to 5.0;

(4) the cis-polybutadiene rubber which is the matrix component of said vinyl-cis-polybutadiene rubber has a 1,4-cis-structure content in the range of 80 % or more;

(5) the 1,2-polybutadiene and the high-molecular substance are dispersed in a physically and/or chemically adsorbed state in the cis-polybutadiene rubber which is the matrix component of said vinyl-cis-polybutadiene rubber; and

(6) the high-molecular substance in said vinyl-cis-polybutadiene rubber is a boiling n-hexane insoluble matter.

[Claim 6]

The rubber composition which is a high-hardness compounded rubber composition according to any one of claims 1 to 5, which is characterized that the diene-based rubber (b) other than (a) is a natural rubber and/or polyisoprene.

[Claim 7]

The rubber composition which is a high-hardness compounded rubber composition according to any one of claims 1 to 6, which is characterized that the rubber reinforcing agent is carbon black.

[Designation of Document] Specification

[Title of the Invention] HIGH-HARDNESS COMPOUNDED RUBBER COMPOSITION

[Technical Field]

[0001]

5 The present invention relates to a high-hardness compounded rubber composition and more specifically, to a rubber composition suitable for beads and chafers of tire, which has improved dimensional stability (die swell is small) at the time of extrusion processing or durability while keeping a high hardness. The rubber composition of the invention which is used for a tire can be used for tire members such as cap treads, sidewall, side reinforcing  
10 layers of run flat tire, carcasses, belts, base treads, stiffeners, and inner liners; industrial products such as rubber vibration insulators, hoses, belts, rubber rolls, rubber coolers, and shoe sole rubbers; and other composites, adhesives, plastic modifiers, and so on.

[Background Art]

[0002]

15 Polybutadiene has a so-called microstructure in which a binding segment formed by polymerization at the 1,4-positions (1,4-structure) and a binding segment formed by polymerization at the 1,2-positions (1,2-structure) are copresent in the molecular chain. The 1,4-structure is further classified into a cis-structure and a trans-structure. On the other hand, the 1,2-structure takes a structure containing a vinyl group as a side chain.

20 [0003]

Hitherto, a production process of a vinyl-cis-polybutadiene rubber composition has been carried out in an aromatic hydrocarbon-based solvent such as benzene, toluene, and xylene. When such a solvent is used, since the viscosity of a polymerization solution is high, there were problems in stirring, heat transfer, delivery, and so on, and excessive energy  
25 was required for recovering the solvent.

[0004]

As the foregoing production process, there is known a process in which 1,3-butadiene is subjected to cis-1,4-polymerization in the foregoing inert organic solvent by using a catalyst obtainable from water, a soluble cobalt compound and an organoaluminum chloride  
30 represented by the general formula,  $AlR_nX_{3-n}$  (wherein R represents an alkyl group having from 1 to 6 carbon atoms, a phenyl group, or a cycloalkyl group; X represents a halogen atom; and  $\underline{n}$  represents a numeral of from 1.5 to 2) to produce BR, and 1,3-butadiene is then subjected to syndiotactic 1,2-polymerization (hereinafter abbreviated as "1,2-polymerization") in the presence of a catalyst obtainable from a soluble cobalt compound, an organoaluminum  
35 compound represented by the general formula,  $AlR_3$  (wherein R represents an alkyl group

having from 1 to 6 carbon atoms, a phenyl group or a cycloalkyl group) and carbon disulfide by adding or not adding 1,3-butadiene and/or the foregoing solvent to this polymerization system (see, for example, JP-B-49-17666 (Patent Document 1) and JP-B-49-17667 (Patent Document 2)).

5 [0005]

Furthermore, for example, JP-B-62-171 (Patent Document 3), JP-B-63-36324 (Patent Document 4), JP-B-2-37927 (Patent Document 5), JP-B-2-38081 (Patent Document 6) and JP-B-3-63566 (Patent Document 7) describe a process in which the production is carried out by subjecting 1,3-butadiene to cis-1,4-polymerization in the presence or absence of carbon  
10 disulfide, or after the production, 1,3-butadiene and carbon disulfide are separated and recovered, thereby circulating 1,3-butadiene not substantially containing carbon disulfide or the foregoing inert organic solvent. In addition, JP-B-4-48815 (Patent Document 8) describes a rubber composition having excellent tensile stress and flex crack growth resistance, in which a compounded material thereof has a small die swell ratio and a  
15 vulcanizate thereof is suitable as a sidewall of tire.

[0006]

Furthermore, JP-A-2000-44633 (Patent Document 9) describes a process in which the production is carried out in an inert organic solvent containing, as the major component, a C4 fraction such as n-butane, cis-2-butene, trans-2-butene, and butene-1. It is described that in  
20 this process, 1,2-polybutadiene contained in the rubber composition is a short fiber crystal, and the distribution of the major axis length of the short fiber crystal is such that 98 % or more of the fiber length is less than 0.6  $\mu\text{m}$  and 70 % or more thereof is less than 0.2  $\mu\text{m}$ . Also, it is described that in the resulting rubber composition, the moldability, tensile stress, tensile strength and flex crack growth resistance of a cis-1,4-polybutadiene rubber (hereinafter  
25 abbreviated as "BR") are improved. However, rubber compositions in which various characteristics are improved were demanded depending upon the utility.

[0007]

Patent Document 1: JP-B-49-17666

Patent Document 2: JP-B-49-17667

30 Patent Document 3: JP-B-62-171

Patent Document 4: JP-B-63-36324

Patent Document 5: JP-B-2-37927

Patent Document 6: JP-B-2-38081

Patent Document 7: JP-B-3-63566

35 Patent Document 8: JP-B-4-48815

[0008]

As rubber members to be disposed in the surroundings of tire bead, high-hardness rubbers are used. Examples thereof include a rubber composition having an increased  
5 compounding amount of carbon black and a rubber composition having a novolak-type phenol resin compounded therein (see JP-B-57-30856) and a rubber composition having short fibers and an olefin-based resin compounded therein (see JP-A-7-315014).

[0009]

With respect to a method for obtaining a high-hardness rubber composition, it is  
10 general to increase carbon black or to compound a fiber, a resin, etc. However, in all of these methods, there may be the case where the heat generation at the time of repeated deformation becomes large, whereby the durability and fatigue resistance are lowered. Thus, improvements are required.

[Disclosure of the Invention]

15 [Problems to be solved by the Invention]

[0010]

An object of the invention is to provide a rubber composition capable of improving dimensional stability at the time of extrusion processing and durability with respect to a tire thereof while keeping a high hardness.

20 [Means for Solving the Problems]

[0011]

The invention is concerned with a rubber composition which is a high-hardness compounded rubber composition comprising 100 parts by weight of a rubber component made of (a) from 20 to 80 % by weight of a vinyl-cis-polybutadiene rubber containing 1,2-  
25 polybutadiene having a melting point of 170 °C or higher and a high-molecular substance having at least one unsaturated double bond per a repeating unit and comprising at least one member selected from polyisoprene, crystalline polybutadiene having a melting point of not higher than 150 °C, liquid polybutadiene and derivatives thereof and (b) from 80 to 20 % by weight of a diene-based rubber other than (a); and (c) from 60 to 100 parts by weight of a  
30 rubber reinforcing agent, which is characterized in that the 1,2-polybutadiene is dispersed in a short crystalline fiber state and the high-molecular substance is dispersed in a granular state in the cis-polybutadiene rubber which is a matrix component of said vinyl-cis-polybutadiene rubber (a); and that the short crystalline fiber of the 1,2-polybutadiene is dispersed in particles of the high-molecular substance.

35 [0012]



Also, the invention is concerned with the rubber composition which is a high-hardness compounded rubber composition, which is characterized in that said vinyl-cis-polybutadiene rubber (a) is produced by a process for producing a vinyl-cis-polybutadiene rubber by subjecting 1,3-butadiene to cis-1,4-polymerization in a hydrocarbon-based solvent by using a cis-1,4-polymerization catalyst, subsequently making a 1,2-polymerization catalyst copresent in the resulting polymerization reaction mixture to subject the 1,3-butadiene to 1,2-polymerization, thereby forming 1,2-polybutadiene having a melting point of 170 °C or higher, and then separating, recovering and obtaining a vinyl-cis-polybutadiene rubber as formed from the resulting polymerization reaction mixture, which is characterizing by including a step for adding a high-molecular substance having at least one unsaturated double bond per a repeating unit within the production system of the vinyl-cis-polybutadiene rubber.

[0013]

Also, the invention is concerned with the rubber composition which is a high-hardness compounded rubber composition, which is characterized in that in the production step of the vinyl-cis-polybutadiene rubber (a), the unsaturated high-molecular substance is contained in the range of from 0.01 to 50 % by mass based on the total sum of the crystalline fiber of 1,2-polybutadiene and the cis-polybutadiene rubber.

[0014]

Also, the invention is concerned with the rubber composition which is a high-hardness compounded rubber composition, which is characterized in that the short fiber of 1,2-polybutadiene in said vinyl-cis-polybutadiene rubber (a) is also dispersed in the cis-polybutadiene rubber as the matrix component without being contained in the particles of the high-molecular substance; that the major axis length of the short crystalline fiber dispersed in said matrix is in the range of from 0.2 to 1,000  $\mu\text{m}$ ; and that the major axis length of the short crystalline fiber of the 1,2-polybutadiene dispersed in the particles of said high-molecular substance is in the range of from 0.01 to 0.5  $\mu\text{m}$ .

[0015]

Also, the invention is concerned with the rubber composition which is a high-hardness compounded rubber composition, which is characterized that said vinyl-cis-polybutadiene rubber (a) has the following characteristics:

(1) the cis-polybutadiene rubber which is the matrix component of said vinyl-cis-polybutadiene rubber has a Mooney viscosity in the range of from 10 to 50;

(2) the cis-polybutadiene rubber which is the matrix component of said vinyl-cis-polybutadiene rubber has a viscosity in a toluene solution at 25 °C in the range of from 10 to 150;

(3) the cis-polybutadiene rubber which is the matrix component of said vinyl-cis-polybutadiene rubber has an  $[\eta]$  in the range of from 1.0 to 5.0;

(4) the cis-polybutadiene rubber which is the matrix component of said vinyl-cis-polybutadiene rubber has a 1,4-cis-structure content in the range of 80 % or more;

5 (5) the 1,2-polybutadiene and the high-molecular substance are dispersed in a physically and/or chemically adsorbed state in the cis-polybutadiene rubber which is the matrix component of said vinyl-cis-polybutadiene rubber; and

(6) the high-molecular substance in said vinyl-cis-polybutadiene rubber is a boiling n-hexane insoluble matter.

10 [0016]

Also, the invention is concerned with the rubber composition which is a high-hardness compounded rubber composition, which is characterized that the diene-based rubber (b) other than (a) is a natural rubber and/or polyisoprene.

[0017]

15 Also, the invention is concerned with the rubber composition which is a high-hardness compounded rubber composition, which is characterized that the rubber reinforcing agent is carbon black.

[Advantages of the Invention]

[0018]

20 The high-hardness compounded rubber composition according to the invention improves dimensional stability at the time of processing and durability of tire at the same time while keeping a high hardness and is able to make the both performances compatible with each in a good balance.

[Best Mode for Carrying Out the Invention]

25 [0019]

In general, the vinyl-cis-polybutadiene rubber (a) of the invention is constructed as follows. That is, it is composed of (1) from 1 to 50 parts by mass of 1,2-polybutadiene having a melting point of 170 °C or higher, (2) 100 parts by mass of a cis-polybutadiene rubber, and (3) from 0.01 to 50 % by mass, based on the whole amount of the foregoing (1) and (2), of an unsaturated high-molecular substance. Furthermore, the 1,2-polybutadiene having a melting point of 170 °C or higher which is the component (1) forms a crystalline fiber in a short fiber state in which a minor axis length of average monodispersed fiber crystals is not more than 0.2  $\mu\text{m}$ , an aspect ratio is not more than 10, and the number of average monodispersed fiber crystals is 10 or more.

35 [0020]

It is desired that the crystalline fiber of 1,2-polybutadiene which is the foregoing component (1) is in a short fiber state in which a minor axis length of average monodispersed fiber crystals is not more than 0.2  $\mu\text{m}$ , and preferably not more than 0.1  $\mu\text{m}$ , an aspect ratio is not more than 10, and preferably not more than 8, and the number of average monodispersed fiber crystals is 10 or more, and preferably 15 or more, and has a melting point of 170  $^{\circ}\text{C}$  or higher, and preferably from 190 to 220  $^{\circ}\text{C}$ .

[0021]

Then, in the vinyl-cis-polybutadiene rubber (a) of the invention, the 1,2-polybutadiene having a melting point of 170  $^{\circ}\text{C}$  or higher which is the foregoing component (1) is present in a short crystalline fiber state and the unsaturated high-molecular substance which is the foregoing component (3) is present in a granular state in the cis-polybutadiene which is the foregoing component (2) as a matrix component. Furthermore, the particle of the unsaturated high-molecular substance as dispersed in the cis-polybutadiene which is the foregoing component (2) as a matrix component has a major axis size in the range of from 0.2 to 1,000  $\mu\text{m}$ , and the short crystalline fiber of the 1,2-polybutadiene as dispersed in the particles of the subject high-molecular substance has a major axis length in the range of from 0.01 to 0.5  $\mu\text{m}$ .

[0022]

It is desired that the cis-polybutadiene rubber which is the foregoing component (2) has the following characteristic. That is, the Mooney viscosity ( $\text{ML}_{1+4}$  at 100  $^{\circ}\text{C}$ , hereinafter abbreviated as "ML") is preferably from 10 to 50, and preferably from 10 to 40. In this way, there are brought such effects that the workability at the time of compounding is improved and the dispersibility of the foregoing component (1) into the component (2) is improved. Furthermore, it is desired that the cis-polybutadiene rubber which is the component (2) has the following characteristics. That is, it is desired that the viscosity in a toluene solution (centipoises at 25  $^{\circ}\text{C}$ , hereinafter abbreviated as "T-cp") is preferably from 10 to 150, and more preferably from 10 to 100; and that  $[\eta]$  (inherent viscosity) is from 1.0 to 5.0, and preferably from 1.0 to 4.0. Furthermore, it is desired that 1,4-cis-structure content is 80 % or more, and preferably 90 % or more; and that a gel matter is not substantially contained. Here, what a gel matter is not substantially contained means that a toluene insoluble matter is not more than 0.5 % by mass.

[0023]

The "toluene insoluble matter" as referred to herein means a gel matter as attached to a 200-mesh wire net after charging 10 g of a sample rubber and 400 mL of toluene in an Erlenmeyer flask, completely dissolving at RT (25  $^{\circ}\text{C}$ ) and then filtering the solution by using

a filter on which the wire net is placed. The foregoing proportion refers to a value as defined in terms of percentage to the sample rubber, which is obtained by drying in vacuo the wire net having a gel attached thereonto and measuring the attachment amount.

[0024]

Furthermore, the  $[\eta]$  (inherent viscosity) is a value  $[\eta]$  as determined according to the following expressions after charging 0.1 g of a sample rubber and 100 mL of toluene in an Erlenmeyer flask, completely dissolving at 30 °C, charging 10 mL of the solution in a Cannon-Fenske dynamic viscometer in a constant-temperature water tank controlled at 30 °C and measuring a drop time (T) of the solution.

$$\eta_{sp} = T/T_0 - 1 \quad (T_0: \text{drop time of only toluene})$$

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c$$

( $\eta_{sp}$ : specific viscosity,  $k'$ : Huggins' constant (0.37),  $c$ : sample concentration (g/mL))

[0025]

It is desired that with respect to the proportion of the 1,2-polybutadiene crystalline fiber which is the foregoing component (1) to the cis-polybutadiene rubber which is the component (2), the proportion of the 1,2-polybutadiene crystalline fiber which is the foregoing component (1) is from 1 to 50 parts by mass, and preferably from 1 to 30 parts by mass based on 100 parts by mass of the cis-polybutadiene rubber which is the component (2) as described previously. When the proportion falls within the foregoing range, it is possible to avoid such inconveniences that in the case where the proportion is large as more than 50 parts by mass, the short fiber crystal of the 1,2-polybutadiene crystalline fiber in the cis-polybutadiene rubber is liable to become large to have poor dispersibility and that in the case where the proportion is small as less than 1 part by mass, the reinforcing properties due to the short fiber crystal are lowered. Accordingly, the problems that the elastic modulus, extrusion processability, moldability and the like as the characteristic features are hardly revealed and that the processability is deteriorated are hardly caused, and therefore, such is preferable. Furthermore, it is desired that the proportion of the unsaturated high-molecular substance which is the component (3) is from 0.01 to 50 % by mass, and preferably from 0.01 to 30 % by mass based on the vinyl-cis-polybutadiene rubber as described previously. What the proportion falls within the foregoing range is preferable in view of an improvement of the dispersibility due to coagulation of the 1,2-polybutadiene crystalline fiber which is the foregoing component (1) and inhibition in lowering of accompanied various physical properties which are derived from the vinyl-cis-polybutadiene rubber, and so on.

[0026]

For example, the foregoing vinyl-cis-polybutadiene rubber is suitably obtained by the following production process.

[0027]

In general, in the production of the vinyl-cis-polybutadiene rubber of the invention,  
5 the polymerization of 1,3-butadiene is carried out by using a hydrocarbon-based solvent. As  
this hydrocarbon-based solvent, a hydrocarbon-based solvent having a solubility parameter  
(hereinafter abbreviated as "SP value") of not more than 9.0 is preferable, and a hydrocarbon-  
based solvent having a solubility parameter of not more than 8.4 is more preferable.  
Examples of the hydrocarbon-based solvent having a solubility parameter of not more than  
10 9.0 include aliphatic hydrocarbons and alicyclic hydrocarbons such as n-hexane (SP value:  
7.2), n-pentane (SP value: 7.0), n-octane (SP value: 7.5), cyclohexane (SP value: 8.1), and n-  
butane (SP value: 6.6). Of these, cyclohexane or the like is preferable.

[0028]

The SP values of these solvents are known by documents such as *Rubber Industry*  
15 *Handbook* (Fourth Edition, The Society of Rubber Industry, Japan, issued January 20, 1994,  
page 721).

[0029]

By using a solvent having an SP value of less than 9.0, the dispersion state of the short  
fiber crystal of the 1,2-polybutadiene crystalline fiber into the cis-polybutadiene rubber is  
20 formed as expected in the invention and an excellent die swell characteristic and high elastic  
modulus and tensile strength are revealed, and therefore, such is preferable.

[0030]

First of all, 1,3-butadiene and the foregoing solvent are mixed, and the water content  
in the resulting solution is then adjusted. The water content is preferably in the range of  
25 from 0.1 to 1.0 mole, and especially preferably from 0.2 to 1.0 mole per mole of the  
organoaluminum chloride used as the after-mentioned cis-1,4-polymerization catalyst in the  
foregoing solution. What the water content falls within this range is preferable because the  
sufficient catalytic activity can be obtained; the preferable content of the cis-1,4-structure and  
the molecular weight can be obtained; the formation of a gel at the time of polymerization can  
30 be inhibited so that attachment of the gel to a polymerization tank or the like can be  
prevented; and in addition, the continuous polymerization time can be prolonged. As a  
method for adjusting the water content, known methods can be applied. A method for  
undergoing addition and dispersion by passing through a porous filtering material (see JP-A-  
4-85304) is also effective.

35 [0031]

An organoaluminum chloride is added as one of the cis-1,4-polymerization catalysts to the solution obtained by adjusting the water content. As the organoaluminum chloride, a compound represented by the general formula,  $\text{AlR}_n\text{X}_{3-n}$  is preferably used. As specific examples thereof, diethylaluminum monochloride, diethylaluminum monobromide, diisobutylaluminum monochloride, dicyclohexylaluminum monochloride, diphenylaluminum monochloride, diethylaluminum sesquichloride, and the like can be suitably enumerated. The amount of use of the organoaluminum chloride is preferably 0.1 mmols or more, and more preferably from 0.5 to 50 mmols per mole of the whole amount of the 1,3-butadiene.

[0032]

Next, a soluble cobalt compound is added as one of other cis-1,4-polymerization catalysts to the mixed solution having an organoaluminum chloride added thereto, thereby subjecting the 1,3-dibutadiene to cis-1,4-polymerization. The soluble cobalt compound is a cobalt compound which is soluble in a hydrocarbon-based solvent to be used or is soluble in liquid 1,3-butadiene, or is able to be uniformly dispersed. Examples thereof include  $\beta$ -diketone complexes of cobalt such as cobalt(II) acetylacetonate and cobalt(III) acetylacetonate;  $\beta$ -keto-acid ester complexes of cobalt such as a cobalt ethylacetoacetate complex; cobalt salts of an organic carboxylic acid having 6 or more carbon atoms such as cobalt octoate, cobalt naphthenate, and cobalt benzoate; and halogenated cobalt complexes such as a cobalt chloride pyridine complex and a cobalt chloride ethyl alcohol complex. The amount of the soluble cobalt compound to be used is 0.001 mmols or more, and especially preferably 0.005 mmols or more based on one mole of 1,3-butadiene. Furthermore, a molar ratio of the organoaluminum chloride to the soluble cobalt compound (Al/Co) is 10 or more, and especially preferably 50 or more. Moreover, in addition to the soluble cobalt compound, an organic carboxylic acid salt of nickel, an organic complex salt of nickel, an organolithium compound, an organic carboxylic acid salt of neodymium, and an organic complex salt of neodymium can be used.

[0033]

The temperature at which the cis-1,4-polymerization is carried out is generally from a temperature exceeding 0 °C to 100 °C, preferably from 10 to 100 °C, and more preferably from 20 to 100 °C. The polymerization time (average residence time) is preferably in the range of from 10 minutes to 2 hours. It is preferred to carry out the cis-1,4-polymerization such that the polymer concentration after the cis-1,4-polymerization is from 5 to 26 % by mass. As the polymerization tank, a single tank is used or two or more tanks are connected and used. The polymerization is carried out by stirring and mixing the solution within the polymerization tank (polymerizer). As the polymerization tank used for the polymerization,

a polymerization tank equipped with a high-viscosity solution stirring unit, for example, a device as described in JP-B-40-2645 can be employed.

[0034]

5 In the production of the vinyl-cis-polybutadiene rubber of the invention, at the time of the cis-1,4-polymerization, a known molecular weight modifier, for example, non-conjugated dienes such as cyclooctadiene, allene, and methylallene (1,2-butadiene); and  $\alpha$ -olefins such as ethylene, propylene, and butene-1 can be used. Furthermore, in order to further inhibit the formation of a gel at the time of the polymerization, a known gelation preventing agent can be used. Furthermore, in general, the content of the cis-1,4-structure in the polymerization  
10 product is 80 % or more, and preferably 90 % or more, and the ML is from 10 to 50, and preferably from 10 to 40. A gel matter is not substantially contained.

[0035]

Then, by adding an organoaluminum compound represented by the general formula,  $AlR_3$  and carbon disulfide and optionally, the foregoing soluble cobalt compound as 1,2-  
15 polymerization catalysts to the thus obtained cis-1,4-polymerization reaction mixture, the 1,3-butadiene is subjected to 1,2-polymerization, thereby producing a vinyl-cis-polybutadiene rubber. On this occasion, the unreacted 1,3-butadiene may be reacted by adding or not adding 1,3-butadiene to the subject polymerization reaction mixture. Suitable examples of the organoaluminum compound represented by the general formula,  $AlR_3$  include  
20 trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, and triphenylaluminum. The amount of the organoaluminum compound is 0.1 mmols or more, and especially from 0.5 to 50 mmols or more per mole of the 1,3-butadiene. Though the carbon disulfide is not particularly limited, water-free carbon disulfide is preferable. The concentration of the carbon disulfide is not more than 20 mmols/L, and especially preferably  
25 from 0.01 to 10 mmols/L. As a replacement of the carbon disulfide, known phenyl isothiocyanate and xanthogenic acid compounds may be used.

[0036]

The temperature at which the 1,2-polymerization is carried out is generally from 0 to 100 °C, preferably from 10 to 100 °C, and more preferably from 20 to 100 °C. In the 1,2-  
30 polymerization, by adding from 1 to 50 parts by mass, and preferably from 1 to 20 parts by mass, based on 100 parts by mass of the foregoing cis-1,4-polymerization reaction mixture, of 1,3-butadiene to the polymerization system, the yield of 1,2-polybutadiene at the time of the 1,2-polymerization can be increased. The polymerization time (average residence time) is preferably in the range of from 10 minutes to 2 hours. It is preferred to carry out the 1,2-  
35 polymerization such that the polymer concentration after the 1,2-polymerization is from 9 to

29 % by mass. As the polymerization tank, a single tank is used or two or more tanks are connected and used. The polymerization is carried out by stirring and mixing the polymerization solution within the polymerization tank (polymerizer). With respect to the polymerization tank which is used for the 1,2-polymerization, since the viscosity becomes  
5 high during the 1,2-polymerization so that the polymer is liable to attach thereto, a polymerization tank equipped with a high-viscosity solution stirring unit, for example, a device as described in JP-B-40-2645 can be employed.

[0037]

10 In the production of the vinyl-cis-polybutadiene rubber of the invention, when the vinyl-cis-polybutadiene rubber is produced by carrying out the cis-1,4-polymerization and subsequently the 1,2-polymerization as described previously, there is included a step for adding a high-molecular substance having at least one unsaturated double bond per a repeating unit and comprising at least one member selected from polyisoprene, crystalline polybutadiene having a melting point of not higher than 150 °C, liquid polybutadiene and  
15 derivatives thereof within the production system of the vinyl-cis-polybutadiene rubber. After the production of a vinyl-cis-polybutadiene rubber, for example, even when such a substance is added at the time of compounding, the effects of the invention of this application are not obtained. With respect to the addition of this unsaturated high-molecular substance within the production system, the addition in the polymerization reaction mixture is  
20 preferably carried out at an arbitrary point of time of from the cis-1,4-polymerization to the 1,2-polymerization, and more preferably at the time of the 1,2-polymerization.

[0038]

As the foregoing unsaturated high-molecular substance, at least one member selected from polyisoprene, crystalline polybutadiene having a melting point of lower than 170 °C,  
25 linear polybutadiene, and derivatives thereof is preferable.

[0039]

Examples of the polyisoprene include usually synthetic polyisoprene (for example, cis-1,4-polyisoprene in which the content of the cis-structure is 90 % or more), liquid polyisoprene, trans-polyisoprene, and other modified polyisoprene.

30 [0040]

The crystalline polybutadiene having a melting point of lower than 170 °C is preferably crystalline polybutadiene having a melting point of from 0 to 150 °C, and examples thereof include low-melting point 1,2-polybutadiene and trans-polybutadiene.

[0041]



Examples of the liquid polybutadiene include extremely low-molecular polybutadiene having an inherent viscosity  $[\eta]$  of not more than 1.

[0042]

Furthermore, examples of these derivatives include an isoprene/isobutylene  
5 copolymer, an isoprene/styrene copolymer, a styrene/isoprene/styrene block copolymer, liquid epoxidized polybutadiene, liquid carboxyl-modified polybutadiene, and hydrogenation products of these derivatives.

[0043]

Of the foregoing respective unsaturated high-molecular substances, isoprene, a  
10 styrene/isoprene/styrene block copolymer, and 1,2-polybutadiene having a melting point of from 70 to 110 °C are preferably used. Further, the foregoing respective unsaturated high-molecular substances can be used singly in admixture of two or more kinds thereof.

[0044]

As described previously, when the foregoing unsaturated high-molecular substance is  
15 added, in the resulting vinyl-cis-polybutadiene rubber, the dispersibility of 1,2-polybutadiene having a melting point of 170 °C or higher into the cis-polybutadiene rubber as a matrix component is remarkably enhanced due to a compatible effect of the unsaturated high-molecular substance. As a result, the characteristics of the resulting vinyl-cis-polybutadiene rubber become excellent.

20 [0045]

The amount of addition of the unsaturated high-molecular substance is preferably in the range of from 0.01 to 50 % by mass, and more preferably from 0.01 to 30 % by mass based on the vinyl-cis-polybutadiene rubber to be obtained. Furthermore, with respect to the addition at any point of time, after the addition, stirring is preferably carried out for from 10  
25 minutes to 3 hours, and more preferably from 10 minutes to 30 minutes.

[0046]

After the polymerization reaction has reached a predetermined rate of polymerization, a known antioxidant can be added according to the usual way. Representative examples of the antioxidant include phenol-based antioxidants such as 2,6-di-t-butyl-p-cresol (BHT);  
30 phosphorus-based antioxidants such as trinonylphenyl phosphite (TNP); and sulfur-based antioxidants such as 4,6-bis(octylthiomethyl)-o-cresol and dilauryl-3,3'-thiodipropionate (TPL). The antioxidant may be used singly or in combination of two or more kinds thereof. The amount of addition of the antioxidant is from 0.001 to 5 parts by mass based on 100 parts by mass of vinyl-cis-polybutadiene rubber. Next, a short stop agent is added to the  
35 polymerization system, thereby stopping the polymerization. This is carried out by a method

which is known by itself, for example, a method in which after completion of the polymerization reaction, the polymerization reaction mixture is fed into a short stop tank and a large amount of a polar solvent such as alcohols such as methanol and ethanol and water is charged in this polymerization reaction mixture; and a method in which an inorganic acid  
5 such as hydrochloric acid and sulfuric acid, an organic acid such as acetic acid and benzoic acid, or a hydrogen chloride gas is introduced into the polymerization reaction mixture. Next, the formed vinyl-cis-polybutadiene rubber is separated, recovered, washed and dried to obtain the desired vinyl-cis-polybutadiene rubber according to the usual way.

[0047]

10 In general, in the thus obtained vinyl-cis-polybutadiene rubber of the invention, the ratio of the respective components, namely the ratio of the 1,2-polybutadiene having a melting point of 170 °C or higher, the cis-polybutadiene rubber and the unsaturated high-molecular substance is as described previously. Furthermore, in the microstructure of the cis-polybutadiene rubber, 80 % or more thereof is occupied by cis-1,4-polybutadiene, and the  
15 remainder consists of trans-1,4-polybutadiene and vinyl-1,2-polybutadiene. This cis-polybutadiene rubber and the unsaturated high-molecular substance are a boiling n-hexane soluble matter, and the 1,2-polybutadiene having a melting point of 170 °C or higher is a boiling n-hexane insoluble matter (hereinafter abbreviated as "H.I."). In general, this 1,2-polybutadiene having a melt point of 170 °C or higher has a melting point of from 170 to 220  
20 °C and is a crystalline fiber in a short fiber state as described previously. Furthermore, as described previously, the ML of the cis-polybutadiene rubber is from 10 to 50, and preferably from 20 to 40.

[0048]

25 Furthermore, as described previously, in the vinyl-cis-polybutadiene rubber of the invention, the 1,2-polybutadiene having a melting point of 170 °C or higher and the unsaturated high-molecular substance are uniformly dispersed in the matrix of the cis-polybutadiene rubber.

[0049]

30 In general, in the vinyl-cis-polybutadiene rubber of the invention, as described previously, the 1,2-polybutadiene having a melting point of 170 °C or higher is dispersed as a crystalline fiber. Furthermore, the unsaturated high-molecular substance can be dispersed in an embodiment of every kind in relation to the crystalline fiber of the 1,2-polybutadiene having a melting point of 170 °C or higher. Examples of this dispersion embodiment include an embodiment in which a crystalline fiber 2 of 1,2-polybutadiene having a melting  
35 point of 170 °C or higher and a fine particle 3 of an unsaturated high-molecular substance are

individually dispersed in a matrix 1 as conceptually shown in Fig. 1; an embodiment in which a fine particle 3 of an unsaturated high-molecular substance is dispersed in a matrix 1 in a state that it is attached to a crystalline fiber 2 of 1,2-polybutadiene as conceptually shown in Fig. 2; an embodiment in which a crystalline fiber 2 of 1,2-polybutadiene is dispersed in a matrix 1 in a state that it is attached to a fine particle 3 of an unsaturated high-molecular substance as conceptually shown in Fig. 3; and an embodiment in which a crystalline fiber 2 of 1,2-polybutadiene is dispersed in a matrix 1 in a state that it is included and dispersed in a fine particle 3 of an unsaturated high-molecular substance as conceptually shown in Fig. 4. Embodiments in which two kinds or more of the dispersion states as shown in Figs. 1 to 4 coexist may be employed. In Figs. 1 to 4, 1 stands for a matrix; 2 stands for a crystalline fiber of 1,2-polybutadiene having a melting point of 170 °C or higher; and 3 stands for a fine particle of an unsaturated high-molecular substance.

[0050]

In the production process of the vinyl-cis-polybutadiene rubber of the invention, the 1,3-butadiene and the hydrocarbon-based solvent are separated from a mother liquor of the polymerization reaction mixture which remains after separating and obtaining the formed vinyl-cis-polybutadiene rubber and which contains the unreacted 1,3-butadiene, the hydrocarbon-based solvent and the carbon disulfide and so on usually by distillation; and the carbon disulfide is separated and removed by an adsorption and separation treatment of carbon disulfide or a separation treatment of a carbon disulfide adduct, thereby recovering the 1,3-butadiene and the hydrocarbon-based solvent which do not substantially contain carbon disulfide. Furthermore, 1,3-butadiene and the hydrocarbon-based solvent which do not substantially contain carbon disulfide can also be recovered by recovering the three components from the foregoing mother liquor of the polymerization reaction mixture by distillation and then separating and removing the carbon disulfide by the foregoing adsorption and separation or separation treatment of a carbon disulfide adduct. The thus recovered carbon disulfide and hydrocarbon-based solvent are mixed with 1,3-butadiene as newly replenished and then provided for reuse.

[0051]

According to the foregoing production process of the vinyl-cis-polybutadiene rubber, it is possible to continuously produce the vinyl-cis-polybutadiene rubber of the invention industrially advantageously with excellent operability of the catalyst component and in a high catalytic efficiency. In particular, it is possible to continuously produce the vinyl-cis-polybutadiene rubber industrially advantageously in a high conversion without causing

attachment to an inner wall in the polymerization tank, a stirring blade and other portions where stirring is slow.

[0052]

Then, in order that the thus produced vinyl-cis-polybutadiene rubber reveals excellent  
5 desired characteristics, it is preferable that the 1,2-polybutadiene crystalline fiber as dispersed  
in the vinyl-cis-polybutadiene rubber is partially dispersed in a monodispersed state as a fine  
crystal in the matrix of the cis-polybutadiene rubber and coexists together with the large 1,2-  
polybutadiene crystalline fiber having a coagulation structure. That is, it is preferable that  
the monodispersed 1,2-polybutadiene crystalline fiber in the matrix of the cis-polybutadiene  
10 rubber is in a short fiber state in which a minor axis length of average monodispersed fiber  
crystals is not more than 0.2  $\mu\text{m}$ , an aspect ratio is not more than 10, and the number of  
average monodispersed fiber crystals is 10 or more and has a melting point of 170 °C or  
higher. Furthermore, in addition to the 1,2-polybutadiene crystalline fiber having a melting  
point of 170 °C or higher, it is preferable that the unsaturated high-molecular substance is  
15 dispersed in the matrix of the cis-polybutadiene rubber. It is preferable that this unsaturated  
high-molecular substance has high affinity with the 1,2-polybutadiene crystalline fiber and is  
dispersed in a physically or chemically adsorbed state in the vicinity of the subject crystalline  
fiber in the matrix of the cis-polybutadiene rubber (the dispersion embodiments of Figs. 2 to  
4). As described previously, when the 1,2-polybutadiene crystalline fiber having a melting  
20 point of 170 °C or higher and the unsaturated high-molecular substance coexist and are  
dispersed in the matrix of the cis-polybutadiene rubber, the foregoing various physical  
properties become excellent, and therefore, such is preferable.

[0053]

Next, a high-hardness compounded rubber composition for tire which is used in the  
25 invention is formed by compounding (a) the foregoing vinyl-cis-polybutadiene rubber, (b) a  
diene-based rubber other than (a), and (c) a rubber reinforcing agent.

[0054]

Examples of the foregoing diene-based rubber (b) include a high cis-polybutadiene  
rubber, a low cis-polybutadiene rubber (BR), a natural rubber, a polyisoprene rubber, an  
30 emulsion polymerized or solution polymerized styrene-butadiene rubber (SBR), an ethylene-  
propylene-diene rubber (EPDM), a nitrile rubber (NBR), a butyl rubber (IIR), and a  
chloroprene rubber (CR).

[0055]

Furthermore, derivatives of these rubbers, for example, polybutadiene rubbers  
35 modified with a tin compound and the foregoing rubbers which are subjected to epoxy

modification, silane modification or maleic acid modification can also be used. These rubbers may be used singly or in combination with two or more kinds thereof.

[0056]

As the rubber reinforcing agent which is the component (c) of the invention, examples thereof include, in addition to various carbon blacks, inorganic reinforcing agents such as white carbon, activated calcium carbonate, and ultra-finely divided magnesium silicate; and organic reinforcing agents such as a syndiotactic 1,2-polybutadiene resin, a polyethylene resin, a polypropylene resin, a hi-styrene resin, a phenol resin, lignin, a modified melamine resin, a coumarone-indene resin, and a petroleum resin. Particularly preferably, carbon black having a particle size of not more than 90 nm and having an oil absorption of dibutyl phthalate (DBP) of 70 mL/100 g or more is enumerated, and examples thereof include FEF, FF, GPF, SAF, ISAF, SRF, and HAF.

[0057]

The foregoing respective components are compounded so as to satisfy the condition of 100 parts by weight of a rubber component of from 20 to 80 % by weight of the vinyl-cis-polybutadiene (a) and from 80 to 20 % by weight of the diene-based rubber (b) other than (a) and from 40 to 100 parts by weight of the rubber reinforcing agent (c).

[0058]

When the amount of the foregoing vinyl-cis-polybutadiene is less than the foregoing lower limit, the die swell is large, and a rubber composition having low exothermic characteristics with respect to a vulcanizate thereof is not obtained, whereas when the amount of the vinyl-cis-polybutadiene exceeds the foregoing upper limit, the Mooney viscosity of the composition is excessively high so that the moldability becomes worse. When the amount of the foregoing rubber reinforcing agent is less than the foregoing lower limit, the die swell becomes large, whereas when it exceeds the foregoing upper limit, the Mooney viscosity is excessively high so that kneading becomes difficult, and therefore, such is not preferable.

[0059]

The rubber composition which is a high-hardness compounded rubber composition of the invention is obtained by kneading the foregoing respective components in the usual way by using a Banbury, an open roll, a kneader, a twin-screw kneading machine, etc. The kneading temperature is required to be lower than the melting point of the 1,2-polybutadiene crystal fiber which is contained in the subject vinyl-cis-polybutadiene. When kneading is carried out at a temperature of higher than this melting point of the 1,2-polybutadiene crystal fiber, fine short fibers in the vinyl-cis-polybutadiene are melted and deformed into a spherical particle or the like, and therefore, such is not preferable.

[0060]

In the rubber composition of the invention, if desired, compounding agents which are usually used in the rubber field, such as a vulcanizer, a vulcanization aid, an antioxidant, a filler, a process oil, zinc white, and stearic acid, may be kneaded.

5 [0061]

As the vulcanizer, known vulcanizers such as sulfur, organic peroxides, resin vulcanizers, and metal oxides such as magnesium oxide are useful.

[0062]

10 As the vulcanization aid, known vulcanization aids such as aldehydes, ammonias, amines, guanidines, thioureas, thiazoles, thiurams, dithiocarbamates, and xanthates are useful.

[0063]

Examples of the antioxidant include amine/ketone-based antioxidants, imidazole-based antioxidants, amine-based antioxidants, phenol-based antioxidants, sulfur-based antioxidants, and phosphorus-based antioxidants.

15 [0064]

Examples of the filler include inorganic fillers such as calcium carbonate, basic magnetic carbonate, clay, litharge, and diatomaceous earth; and organic fillers such as regenerated rubbers and powdered rubbers.

[0065]

20 As the process oil, all of aromatic process oils, naphthene-based process oils, and paraffin-based process oils are useful.

[0066]

25 The high-hardness compounded rubber composition of the invention has a small die swell and has a low exothermic characteristic with respect to a vulcanizate thereof. Thus, it can be used as a tire member of passenger automobile, bus, truck, airplane, run flat tire, etc. in combination with other tire member (for example, cap tread, sidewall, sidewall reinforcing layer, base tread, carcass, belt, and bead) in place of the conventionally known high-hardness compounded rubber composition.

[0067]

30 Examples based on the invention and Comparative Examples will be specifically described below. In the Examples and Comparative Examples, physical properties of a raw rubber of the resulting vinyl-cis-polybutadiene rubber, physical properties of a compounded material of the resulting high-hardness compounded rubber composition suitable for beads and chafers, and physical properties of a vulcanizate thereof were measured in the following  
35 manners.

(1) Content of 1,2-polybutadiene crystalline fiber:

An extraction residue resulting from subjecting 2 g of a vinyl-cis-polybutadiene rubber to boiling extraction with 200 mL of n-hexane for 4 hours by a Soxhlet extractor was expressed in terms of parts by weight.

5 (2) Melting point of 1,2-polybutadiene crystalline fiber:

An extraction residue of boiling n-hexane was determined by a peak temperature of the endothermic curve by a differential scanning calorimeter (DSC).

(3) Crystalline fiber form:

10 The vinyl-cis-polybutadiene rubber was vulcanized with sulfur monochloride and carbon disulfide; a vulcanizate was cut out into an ultra-thin section; and the double bond of the rubber segment of the vinyl-cis-polybutadiene was dyed with an osmium tetrachloride vapor and determined by observation by a transmission electron microscope.

(4) Microstructure of rubber segment in vinyl-cis-polybutadiene rubber:

15 An infrared absorption spectral analysis was carried out. The microstructure was calculated from an absorption intensity ratio of cis at  $740\text{ cm}^{-1}$ , trans at  $967\text{ cm}^{-1}$  and vinyl at  $910\text{ cm}^{-1}$ .

(5) Viscosity in toluene solution of rubber segment in vinyl-cis-polybutadiene rubber:

A viscosity in a 5 % by weight toluene solution at  $25\text{ }^{\circ}\text{C}$  was measured and expressed in terms of centipoises (cp).

20 (6)  $[\eta]$  of rubber segment in vinyl-cis-polybutadiene rubber:

A boiling n-hexane soluble matter was collected by drying and measured in a toluene solution at a temperature of  $30\text{ }^{\circ}\text{C}$ .

(7) Mooney viscosity:

A value measured at  $100\text{ }^{\circ}\text{C}$  according to JIS K6300.

25 (8) Die swell:

As an estimation for extrusion processability of a compounded material, a ratio of the size of a compounded material and the die orifice size (wherein  $L/D = 1.5\text{ mm}/1.5\text{ mm}$ ) was measured and determined at the time of extrusion at  $100\text{ }^{\circ}\text{C}$  and at a shear rate of  $100\text{ sec}^{-1}$  by using a processability analyzer (MPT, manufactured by Monsanto).

30 (9) Hardness:

This was measured at room temperature by using a type A durometer according to JIS K6253.

(10) Low fuel consumption (low exothermic characteristics or exothermic characteristic):

A heat build-up of a rubber composition was measured in a fixed stress mode with a static load of 196 N under conditions of a temperature of 40 °C and a frequency of 10 Hz. The smaller the index, the more excellent the fuel consumption is.

[Examples]

5 [0068]

(Production of vinyl-cis-polybutadiene sample 1)

In a stirrer-equipped stainless steel-made reaction tank having an internal volume of 30 L and purged with a nitrogen gas, a solution of 1.6 kg of 1,3-butadiene dissolved in 18 kg of absolute cyclohexane was charged, to which were then added 4 mmoles of cobalt octoate, 10 84 mmoles of diethylaluminum chloride and 70 mmoles of 1,5-cyclooctadiene, and the mixture was stirred at 25 °C for 30 minutes, thereby undergoing cis-polymerization. The resulting polymer had an ML of 33 and a T-cp of 59 and had a microstructure consisting of 0.9 % of the 1,2-structure, 0.9 % of the trans-1,4-structure and 98.2 % of the cis-1,4-structure. After the cis-polymerization, 5 % by mass (percentage based on the resulting vinyl-cis-poly- 15 butadiene rubber) of an unsaturated high-molecular substance consisting of polyisoprene (IR) (ML: 87, cis-1,4-structure: 98 %) was added to the resulting polymerization product solution, and the mixture was stirred at 25 °C for one hour. Immediately thereafter, 90 mmoles of triethylaluminum and 50 mmoles of carbon disulfide were added to the polymerization solution, and the mixture was stirred at 25 °C for 60 minutes, thereby undergoing 1,2- 20 polymerization. After completion of the polymerization, the polymerization product solution was added to 18 L of methanol containing 1 % by mass of 4,6-bis(octylthiomethyl)-o-cresol, thereby depositing and precipitating a rubbery polymer. This rubbery polymer was separated, washed with methanol and then dried in vacuo at the normal temperature. The thus obtained vinyl-cis-polybutadiene rubber had a percent yield of 80 %. Thereafter, this 25 vinyl-cis-polybutadiene rubber was treated with boiling n-hexane, and an insoluble matter and a soluble matter were separated and dried. The resulting boiling n-hexane soluble polymer had an ML of 31, a T-cp of 57 and a T-cp/ML relation of about 1.8 and had a microstructure consisting of 1.0 % of the 1,2-structure, 0.9 % of the trans-1,4-structure and 98.1 % of the cis-1,4-structure. Furthermore, the  $[\eta]$  was 1.7. The number of monodispersed fiber crystals 30 having a minor axis length of not more than 0.2  $\mu\text{m}$ , which were contained in the vinyl-cis-polybutadiene rubber, was 100 or more, the aspect ratio was not more than 10, and the melting point was 202 °C.

[0069]

(Production of vinyl-cis-polybutadiene sample 2)



A vinyl-cis-polybutadiene was obtained in the same manner as in the production process of the sample 1, except for not adding the unsaturated high-molecular substance (additive).

[0070]

5           Physical properties of the foregoing sample 1 and sample 2 are shown in Table 1.

Table 1

Sample Name	Sample 1	Sample 2
High-molecular substance (Amount of addition)	IR (10 % by weight)	Nil
Polymerization solvent (SP value of polymerization solvent)	Cyclohexane 8.1	← ←
Characteristics of matrix in vinyl-cis-polybutadiene rubber	Mooney viscosity	←
	[ $\eta$ ]	1.4
	Viscosity in toluene solution (cp)	←
	Cis	←
	Trans	←
Characteristics of 1,2- polybutadiene crystalline fiber	Microstructure (%)	←
	Vinyl	←
	Melting point of fiber crystal (°C)	←
	Number of monodispersed fiber crystals: (Number of crystals having a minor axis length of not more than $0.2 \mu$ per $400 \mu^2$ )	4
	Aspect ratio of monodispersed fiber crystal	20 or more
% by weight of 1,2-polybutadiene	Major axis size of crystalline fiber dispersed in matrix	1 or more
	Major axis size of crystalline fiber dispersed in high- molecular substance	-
	12	←
Number of monodispersed fiber crystals	Large	Small

[0071]

(Examples 1 to 5) and (Comparative Examples 1 to 4)

By using each of the foregoing sample 1 and sample 2, compounding agents other than a vulcanization accelerator and sulfur in a compounding preparation as shown in Table 2  
5 were kneaded by using a 1.7-L Banbury mixer for testing, thereby obtaining a kneaded material which is a high-hardness compounded rubber composition. On this occasion, a maximum kneading temperature was adjusted at 170 to 180 °C. Next, this kneaded material was kneaded with a vulcanization accelerator and sulfur on a 10-inch roll, and the mixture was rolled in a sheet form and then charged in a die for vulcanization, thereby obtaining a  
10 vulcanizate. The vulcanization was carried out at 150 °C for 30 minutes. The results are summarized and shown in Table 2.

[0072]

The compositions of the Examples are greatly improved with respect to the elastic modulus and highly balanced between the die swell and the low exothermic characteristics.  
15 On the other hand, in the compositions of the Comparative Examples, when the commercially available BR is used, the die swell is large; and when the compounding amount of carbon black is high, the exothermic characteristic is deteriorated. Furthermore, when vinyl-cis-polybutadiene which is not satisfied in the invention is used or the amount of use of vinyl-cis-polybutadiene of the invention is low, the improvement effects did not reached the expected  
20 levels.

[0073]

Table 2

Compounding table	Example						Comparative Example			
	1	2	3	4	5		1	2		
Kind of vinyl-cis-polybutadiene Amount (parts)	Sample 1 50	Sample 1 70	Sample 1 30	Sample 1 50	Sample 1 50		-		Sample 1 50	
NR (Note 1)	50	30	70	50	50		50		50	
BR (Note 2)	-	-	-	-	-		50		-	
Carbon black N330	70	70	70	60	80		70		70	
Aromatic oil	5	5	5	10	10		5		5	
Zinc oxide	5	5	5	3	3		5		5	
Stearic acid	2	2	2	2	2		2		2	
Antioxidant (Note 3)	1	1	1	1	1		1		1	
Vulcanization accelerator (Note 4)	1.0	1.2	0.8	1.0	1.0		1.0		1.0	
Sulfur	3.0	2.8	3.2	3.0	3.0		3.0		3.0	
Physical properties of compounded material:										
Die swell index	75	68	85	83	65		100		89	
Physical properties of vulcanizate										
Hardness (index)	124	134	16	116	130		100		109	
Low exothermic characteristics (index)	80	73	87	68	84		100		104	

(Note 1) NR: RSS#1

(Note 2) BR: Polybutadiene (UBEPOL-BR150, manufacture by Ube Industries, Ltd.)

(Note 3) Ultrasil VN3 GR (manufactured by Degussa)

(Note 4) X50S (Equal-amount mixture of N330 and Si69, manufactured by Degussa)

5 Si69: Bis(3-triethoxysilylpropyl)-tetrasulfide

(Note 5) Antioxidant: ANTAGE AS (a reaction product between amine and ketone)

(Note 6) Vulcanization accelerator: NOCCELER CZ (N-cyclohexyl-2-benzothiazole sulfenamide)

(Note 7) Vulcanization accelerator: NOCCELER D (N,N'-diphenylguanidine)

10 [Brief Description of the Drawings]

[0074]

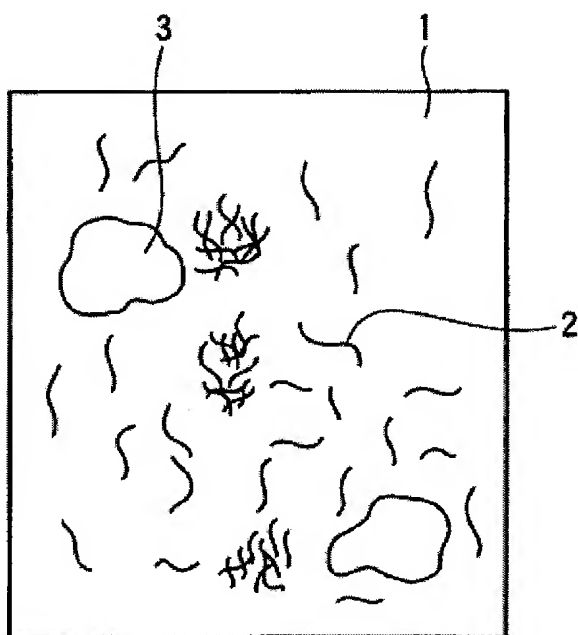
[Fig. 1] shows an embodiment in which a crystalline fiber 2 of 1,2-polybutadiene having a melting point of 170 °C or higher and a fine particle 3 of an unsaturated high-molecular substance are individually dispersed in a matrix 1.

15 [Fig. 2] shows an embodiment in which a fine particle 3 of an unsaturated high-molecular substance is dispersed in a matrix 1 in a state that it is attached to a crystalline fiber 2 of 1,2-polybutadiene.

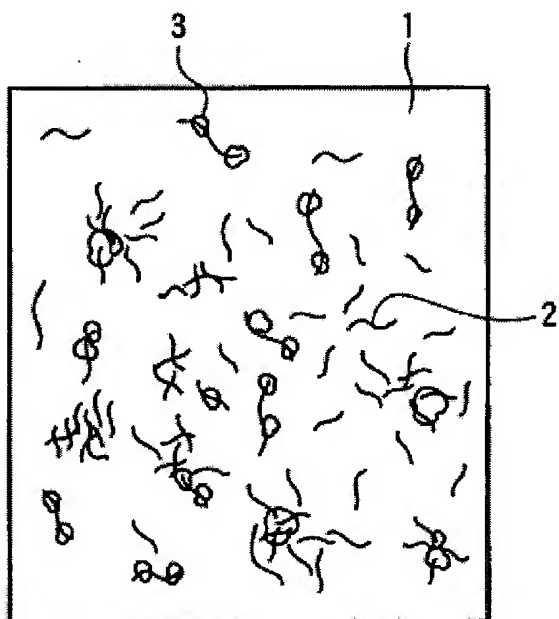
[Fig. 3] shows an embodiment in which a crystalline fiber 2 of 1,2-polybutadiene is dispersed in a matrix 1 in a state that it is attached to a fine particle 3 of an unsaturated high-molecular substance.

20 [Fig. 4] shows an embodiment in which a crystalline fiber 2 of 1,2-polybutadiene is dispersed in a matrix 1 in a state that it is included and dispersed in a fine particle 3 of an unsaturated high-molecular substance.

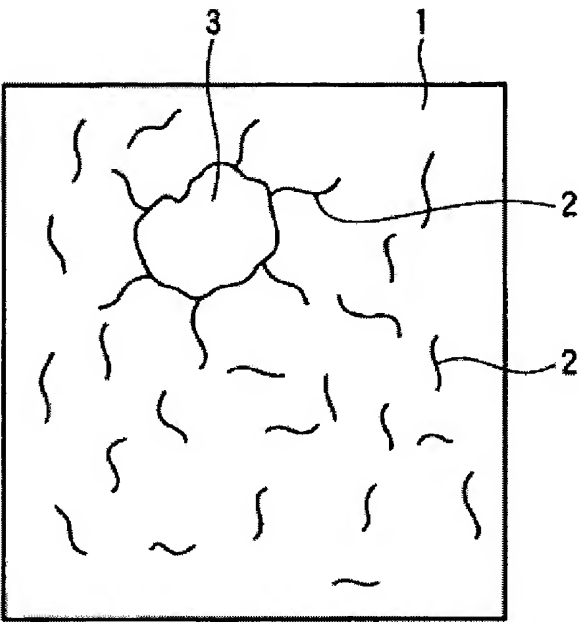
[Fig. 1]



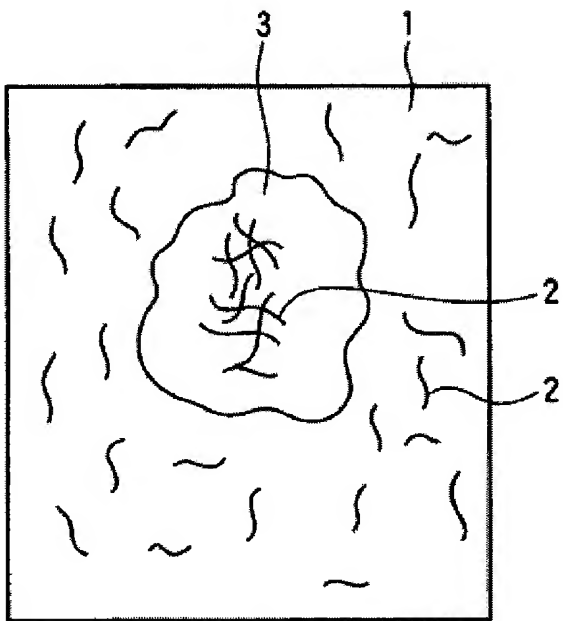
5 [Fig. 2]



[Fig. 3]



[Fig. 4]



[Designation of Document] Abstract

[Abstract]

[Problem]

5 An object is to provide a rubber composition capable of improving dimensional stability at the time of extrusion processing and durability with respect to a tire thereof while keeping a high hardness.

[Means for Solution]

10 It relates to a rubber composition which is a high-hardness compounded rubber composition 1 comprising a rubber component made of a vinyl-cis-polybutadiene rubber containing 1,2-polybutadiene having a melting point of 170 °C or higher, crystalline polybutadiene having a melting point of not higher than 150 °C and the like and a diene-based rubber other than that; and a rubber reinforcing agent, which is characterized in that the 1,2-polybutadiene is dispersed in a short crystalline fiber state and the high-molecular substance is dispersed in a granular state in the cis-polybutadiene rubber which is a matrix component of  
15 said vinyl-cis-polybutadiene rubber ; and that the short crystalline fiber of the 1,2-polybutadiene is dispersed in particles of the high-molecular substance.

[Selected Drawing] Figure 1